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Experimental Observation of Quantum Confinement in the Conduction Band of CdSe Quantum Dots

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Recent theoretical descriptions as to the magnitude of effect that quantum confinement has on the conduction band (CB) of CdSe quantum dots (QD) have been conflicting. In this manuscript, we experimentally identify quantum confinement effects in the CB of CdSe QDs for the first time. Using X-ray absorption spectroscopy, we have unambiguously witnessed the CB minimum shift to higher energy with decreasing particle size and have been able to compare these results to recent theories. Our experiments have been able to identify which theories correctly describe the CB states in CdSe QDs. In particular, our experiments suggest that multiple theories describe the shifts in the CB of CdSe QDs and are not mutually exclusive.

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Semiconductor quantum dots (QDs) are known to exhibit size-dependent optical and electronic properties and, as a consequence, offer considerable potential for a diverse range of technological applications. While changes in the optical properties with QD size can be explained in terms of quantum confinement effects, further study of many nanocrystalline semiconductors is essential if they are to be successfully integrated into new or existing devices. In particular, characterization of the electronic structure remains of fundamental importance in developing a comprehensive understanding of their optical and electronic behavior and, therefore, optimizing functional performance. In this letter, we report the first experimental study of the evolution in the conduction band density of states (CBDOS) of a binary semiconductor QD as a function of particle size. X-ray absorption spectroscopy measurements of the size-dependent CBDOS structure of CdSe QDs are used to explain conflicting results obtained from theoretical calculations based upon quantum confinement effects.

In contrast to many binary semiconductor quantum dots, CdSe QDs are readily synthesized with narrow size distributions and possess excellent photochemical stability when passivated properly. [1, 2] In addition, they demonstrate size dependent photoluminescence that encompasses the visible region of the electromagnetic spectrum. [3] Hence, CdSe represents an archetypal system for numerous QD applications (including uses in biomedical imaging and laser diodes) and an ideal model for the study of quantum confinement effects. Although extensive research has been devoted to characterization of the electronic structure in CdSe QDs, [4–9] the size-dependent evolution of the valence band (VB) and CBDOS remain unresolved from one another via experimental study. It has been demonstrated that theoretical calculations provide a means for the deconvolution and isolated study of the VB and CB. Nonetheless, the results reported for CdSe exhibit strong model dependence,

which is illustrated by predicted scaling laws ranging between $E_c \propto R^{-0.8}$ [10] and R^{-2} [8] for size-dependent energy shifts in the bottom of the CBDOS. As such, identification of the most representative theory is paramount.

Several experimental techniques have been used to address the development of the band gap in nanocrystalline CdSe [3, 5, 11–13] (particularly UV-Visible absorption spectroscopy because it also provides a diagnostic of QD particle size and size dispersion), but the band gap represents only the convolution of the VB and CB and does not allow for an independent treatment of these edges. The application of alternative methods is essential, therefore, for successful mapping of the electronic structure in CdSe QDs. X-ray absorption spectroscopy (XAS) offers the ideal technique with which to resolve the size-dependent evolution of the bottom of the CBDOS because it is both element specific and a probe of the unoccupied density of states. Moreover, selection of the appropriate absorption edge allows one to focus upon the bottom of the CB. The projected DOS obtained from theory demonstrates that the bottom of the CB is comprised of Cd $5s$ states (see Figure 1b). Hence, the Cd L_3 edge should be ideal for probing any size dependent effects in this region because transitions between the $2p$ initial state and unoccupied s states are dipole allowed. If the bottom of the CdSe CB moves by some energy, ΔE_c , then the L_3 absorption edge should shift by a corresponding amount representing the quantum confinement induced shift in the CB. In principle, the Cd M_2 - and M_3 -edges, which are comprised of a $3p$ initial state, could also be used to probe the bottom of the CB. The M -edges, however, suffer from weak signals and a large background which limits the usefulness of using these edges for quantitative information.

CdSe quantum dots (QD) with a mean radius ranging from 9-19 Å and coated with the ligand trioctylphosphine oxide (TOPO) were synthesized using a known method. [1] QD size and size dispersion were derived using UV-Visible absorption spectroscopy. [5] A

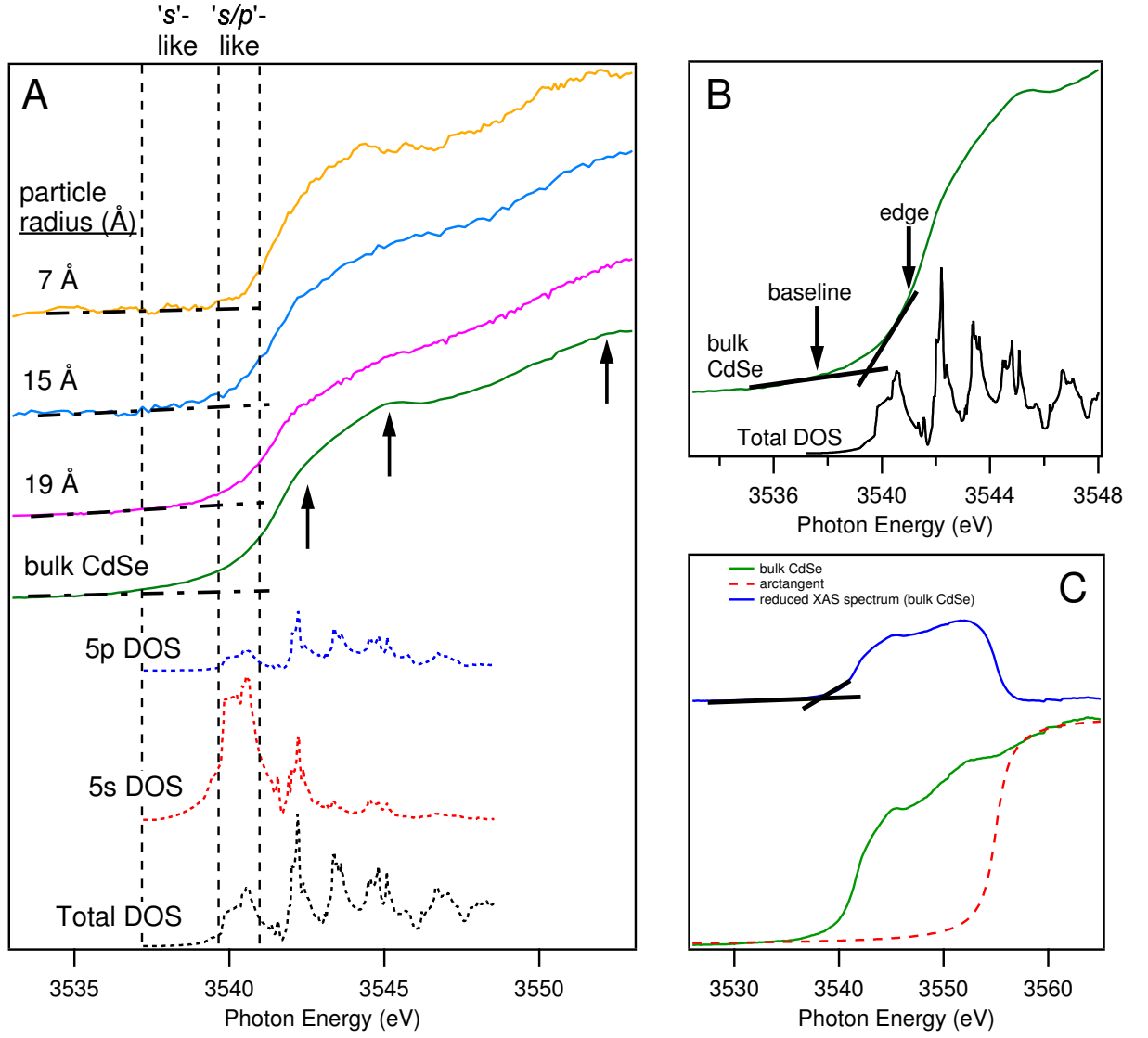


FIG. 1: (A) Calculated conduction band (CB) density of states (DOS) for bulk CdSe with the experimental Cd L_3 -edge XAS spectra. (B) Extrapolation method to derive CB shifts as described in the text. The total DOS are plotted to define the baseline of the experimental spectrum. The edge is defined as the median y -value between the baseline and step edge and a tangential line is drawn along the edge. (C) Arctangent method to derive CB shifts as described in the text. Note the reduction of the sloped pre-edge region which allows for a better defined baseline.

$\text{Cd}_{10}\text{Se}_4(\text{SC}_6\text{H}_5)_{16}^{4-}$ (Cd_{10}) cluster sample was prepared using an established technique. [14] It should be noted that the Cd_{10} cluster has a radius of 7 Å and is not coated with TOPO but with thiophenol. For the XAS measurements, the QDs were deposited from toluene onto a Si(111) wafer and the solvent was allowed to slowly evaporate. Multiple depositions were performed to ensure a sufficiently thick CdSe film was obtained. XAS experiments were performed on the bend magnet beamline 9.3.1 at the Advanced Light Source. The measurements were taken in both total electron and total photon yield without any noticeable differences between the two detection

methods. The current from a gold grid, I_o , was used to normalize the XAS spectra. Although the experimental resolution in these experiments was ~ 0.2 eV with lifetime broadening of ~ 1.0 eV, the accuracy in measurement of the absorption onset energy is considerably better.

Figure 1A plots selected XAS spectra at the Cd L_3 edge for CdSe QDs of different sizes and the corresponding bulk spectrum. To compare the experimental CB-DOS features, we show the calculated CBDOS for bulk CdSe as a dotted line in Figure 1. The calculated projected CBDOS were obtained using a full-potential linear muffin-tin orbital method. [15–17] The angular-

momentum-resolved projected CBDOS were generated on the basis of a Mulliken decomposition and by projecting out against the atom-centered numerical basis functions obtained from the self-consistent calculations. [17–19]

The bulk CdSe L_3 -edge spectrum shows a sharp absorption onset with a distinct foot (Fig. 1A) with absorption features ca. 4, 7, and 14 eV above the onset marked by arrows in Figure 1A. A noticeable difference in the spectral features between bulk CdSe and the QD samples is a reduction of intensity in the foot of the absorption onset. The calculated CBDOS indicate that the foot in the absorption spectrum is due to Cd 5s states and comprises the CB minimum. Therefore, it is necessary to look at this region of the spectrum in order to identify any shifts in the bottom of the CB that may arise from quantum confinement effects. The presence of significant DOS features near the baseline, however, cause some difficulty in obtaining an absolute measure of the absorption onset. The energy of the absorption onset is obtained by extrapolation of the linear region of the baseline and the linear region of the absorption edge above the threshold and identifying the point at which they intersect. A specific protocol was followed to determine where the extrapolated lines are drawn on the spectrum to warrant self-consistent results (and error). The baseline is extrapolated from the linear component of the pre-edge region and is defined to delineate from the experimental data at the energy for which the calculated CBDOS is non-zero. In other words, the baseline of the experimental spectrum ends at the point where DOS features begin and is $\sim 2\sigma$ above baseline noise. The line on the absorption edge begins at the median y -value between the baseline and step edge and from this point, a tangent is drawn to the edge (see Figure 1B). Using this protocol, values of the extrapolation onset can be obtained with minimal contribution from biased error. A second and alternative protocol was introduced which sharpens the DOS features present near the baseline. An arctangent function (Figure 1C) was subtracted from the experimental data which allows a more straightforward analysis of the absorption edge. [20] The arctangent function represents transitions between the $2p$ initial state \rightarrow continuum/free electron states. The values obtained from both data analysis protocols are comparable and indicate that the shifts reported in this letter represent an accurate measure of the evolution of the CB minimum with particle size.

A comparison of the results from the two methods is provided by Figure 2 which displays the CB shifts for the series of CdSe QD samples studied in this letter. For the purposes of direct comparison reported theoretical values [10, 21] have been plotted alongside the data. The reduction of the DOS features in the absorption onset in the QD samples with respect to the bulk CdSe sample is most likely due to quantum confinement induced shifts

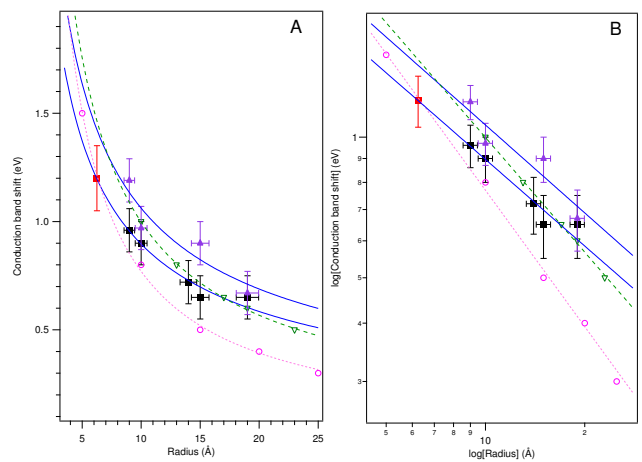


FIG. 2: (A) Size dependent values for the CdSe conduction band states. The \blacksquare and \blacktriangle represent the CdSe QD experimental data points using the extrapolation and arctangent subtraction data analysis methods, respectively, as described in the text, while the ∇ (CP theory; Ref. 10) and \circ (TB theory; Ref. 21) represent theoretical values. The lines through the data points represent a least squares fitting of the data. (B) Same as A, but plotted on a Log-Log scale for better distinction between data points.

in the bottom of the CB edge. As seen from Figure 2, the L_3 -edges of the QD samples are shifted to higher energies relative to bulk CdSe. For example, shifts of 0.65 eV to 1.2 eV are observed for the 19 and 7 Å radius CdSe QD samples respectively, which are consistent with the quantum confinement model. The agreement between experiment and both theories is close, but better agreement is seen with the charge patching (CP) theory [10] at larger particle sizes than with the tight-binding (TB) theory [21]. The CP method, which uses the charge density rather than the local potentials to generate the electronic structure, better represents the experimental system for three reasons: (1) The CP theory is a first-principles theory based on the local density approximation (LDA). In the CP approach, the electronic structure is calculated for a small system (i.e. 10-100 atoms) using LDA. The charge density is then generated for the small system and multiplied in order to produce the charge densities for larger systems. It has been shown that the CP method, when compared to LDA, is accurate on the order of 50 meV error [22] which is smaller than the experimental error. (2) Within the TB theory, a basis set of sp^3s^* was used, which indicates that the calculated conduction band states are comprised of mainly s states with some p state contribution. Although it is believed that shifts will occur from s related states, this basis set gives a relatively crude description of the conduction band. (3) The CP theory includes a hydrogenlike passivation. Although not ideal, it provides a semi-realistic model of the surface.

Consolidation of the plot shown in Figure 2 into a scaling law introduces a means of describing the relevant QD physics in a simple mathematical expression, which is readily compared with theoretical values. For instance, more simplistic theories like the effective mass approximation indicate that the CB shift scaling law should be, $E_c \propto R^{-2}$. More sophisticated theories like the TB method indicate the CB shift to be, $E_c \propto R^{-1.0}$. Experimentally, we observe a CB shift of, $E_c \propto R^{-0.6}$ with an error of ± 0.04 and ± 0.1 for values obtained via the extrapolation and arctangent subtraction, respectively. The scaling law obtained via the CP theory is $E_c \propto R^{-0.8}$ (see Figure 2B). The low error associated with the scaling laws allows the assertion that the experiment demonstrates better agreement with the CP theory than with the TB theory. Despite the close agreement observed in the CB scaling obtained from experiment and CP theory, the small discrepancy between the scaling laws (even with error considered) suggests new physics may occur at small sizes which slows down the shift of the CB. Therefore, we suggest that smaller scaling laws are observed experimentally because a regime is entered at small sizes in which the CBM does not shift with size.

Recent results by Puzder, et al [23] suggest that small CdSe QDs (less than 10 Å radius) do not show a size dependence in the CB; rather, a consistent shift of ~ 1 eV relative to the bulk value is seen for the CBM. Although the differences between the theoretical results presented in this manuscript is difficult to explain, it has been postulated that this is part due to differences in modeling the nanoparticle surface. We believe that the XAS results can be used to explain these contrary theoretical results in terms of a simple quantum confinement argument. The XAS results indicate that there are energy states in the upper conduction band of CdSe QDs that are inherently unaffected by quantum confinement, unlike the states at the bottom of the CB which are strongly affected. As already stated, the CdSe CBDOS are comprised of Cd 5s states at the bottom of the CB, with hybridized 5p/5s state contribution above the CB minimum. In Fig. 1 it is clear that as the particle size is decreased, the s-like states shift to higher energy whereas the states labeled *ps* do not move. For the smallest particle size, it appears that the *s* states have shifted to such a degree that the bottom of the conduction band is now dominated by the hybridized *p* and *s*-like states. This would explain the contradictions between theories and suggest that the reason the CB edge no longer shifts in particles below 10 Å as proposed by Puzder et. al. [23] is that the CB minimum is now composed of hybridized *p* and *s* like states. Band structure calculations (Figure 3A and B) show that the Cd 5s energy bands are parabolic near the CB minimum and are expected to be highly affected by quantum confinement; the *ps* states are flat and should stay localized irrespective of particle size (Figure 3C) although this has not yet been explored

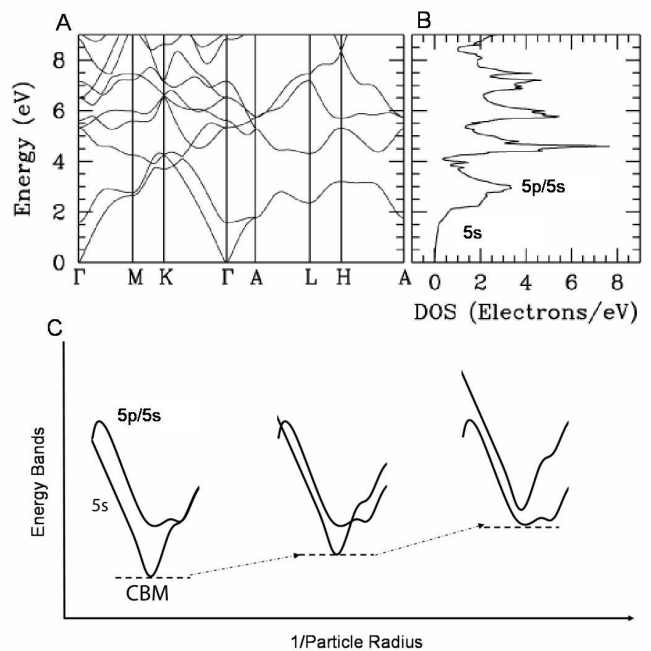


FIG. 3: (A) Calculated bulk CdSe conduction band diagram. (B) Corresponding conduction band density of states (DOS) which emphasizes the correlation of the DOS features with the energy bands. (C) Schematic energy bands depicting movement of the bands as a function of particle size. Notice the parabolic nature of the 5s states at the conduction band minimum versus the 5p/5s states which explains the differences in mobility of the bands with quantum confinement. It must be noted that the *shape* of the bands as a function of particle size is not accurately represented and this illustration is intended only to demonstrate the *mobility* of the bands with particle size.

theoretically. In the case of the 5s states, the observed shifts are similar to those predicted by CP theory for particles larger than ~ 10 Å diameter. For particles less than 10 Å radius, the weak size dependence of the shifts derived from the inflection points indicate that the states at the conduction band minimum are most likely the flat-band *ps* states.

We conclude that contradictory theories in interpreting the quantum confinement induced shift of the conduction band in CdSe quantum dots can be addressed using X-ray absorption spectroscopy. As the CdSe particle size decreases, *s* states in the bottom of the conduction band shift to higher energy due to quantum confinement while hybridized 5p/5s states are unaffected by size. A conduction band comprised of hybridized *ps* states at small particle sizes is proposed. These results suggest that there exists an upper limit to extent the conduction bands of CdSe can shift with particle size and should have impact on the future fabrication of electronic materials based on CdSe.

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